Supplementary Material (ESI) for Dalton Transactions

(η^6-arene) ruthenium(II) complexes and metallo-papain hybrid as Lewis acid catalysts of Diels-Alder reaction in water

Barisa Talbi,[a] Pierre Haquette,[a] Annie Martel,[a] Céline Fosse,[b] Stéphane Cordier,[c] Thierry Roisnel,[c] Gérard Jaouen[a] and Michèle Salmain*[a]

[a] Chimie ParisTech (Ecole Nationale Supérieure de Chimie de Paris), Laboratoire Charles Friedel, CNRS UMR 7223, 11 rue Pierre et Marie Curie 75231 Paris cedex 05, France
[b] Chimie ParisTech (Ecole Nationale Supérieure de Chimie de Paris), Laboratoire de spectrométrie de masse, 11 rue Pierre et Marie Curie 75231 Paris cedex 05, France
[c] Université de Rennes I, UMR CNRS 6226 "Sciences Chimiques de Rennes", Avenue du Général Leclerc 35042 Rennes Cedex, France

SUPPLEMENTARY INFORMATION

A) **Synthesis**

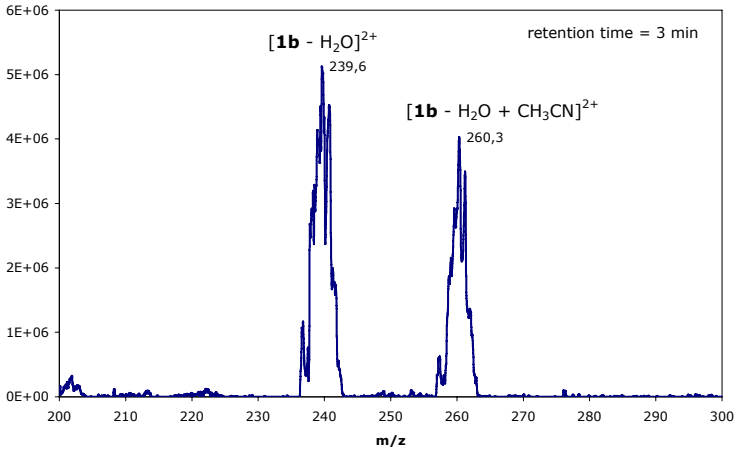
a. Materials

Solvents were dried and distilled by standard procedures and all reactions and manipulations were performed under an inert atmosphere of argon or nitrogen using standard Schlenk and vacuum-line techniques. Flash chromatography was performed on silica gel Merck 60 (40-63 μm). NMR spectra were recorded on a 400 MHz Bruker spectrometer. Compound **1a** was prepared according to ref. [i]. Compounds **2a**, **3a**, **2b** and **3b** were prepared according to ref. [ii] *N*-ethylmaleimide (NEM) was purchased from Pierce (Thermo-Fischer). Papain was purchased from Fluka (ref 76220) and purified by affinity chromatography according to ref. [iii]. The hydrolytic activity of papain, papain-**1a** and papain-NEM was assayed using L-pyroglutamyl-L-phenylalanyl-L-leucine-*p*-nitroanilide (PFLNa) purchased from Bachem in 100 mM phosphate, 300 mM KCl, 0.1 mM EDTA pH 6.5 containing 10% DMSO (v/v).[iv] GC analyses were performed on a CP-3380 gas chromatograph (Varian) equipped with a Chrompack capillary column CP-Chiralsil-Dex CB. Reverse phase HPLC of **1b** was performed with a Nucleosil C8 column (5 um, 4.6 x 250 mm). Species were eluted isocratically with 15 % MeCN-0.1% formic acid in H_2O-0.1% formic acid at 1 ml/min.

*b. [Ru{η^6-C_6H_5-CH_2-CH_2-NH-CO-CH_2Cl}(phen)H_2O]$(BF_4)_2$ **1b***

Compound **1b** was prepared by a procedure adapted from ref. [2]. A mixture of the monocationic complex **1a** (0.0727 mmol, 40 mg) and one equivalent of silver sulphate (0.0727 mmol, 22.7 mg) in water (11 ml) was stirred for 2 h in the dark at room temperature. The white precipitate (AgCl) was removed by canula filtration from the yellow solution. Two equivalents of $NaBF_4$ (0.0727 mmol, 16 mg) were dissolved in the solution. After evaporation of the water, the yellow solid was dissolved in 5 ml of dry acetonitrile and filtered on celite. The solvent was evaporated, and the solid redissolved in water to replace a molecule of acetonitrile coordinated to the metal by a molecule of water. After concentration of the solution and storage at 4°C, the colourless solution was filtered, and the yellow solid was dried under vacuum. Yield: 82 %. ^{1}H NMR (D_2O, 20°C, 400 MHz, Me_4Si) δ (ppm) 9.96 (dd, J = 5.09, J = 1.2 Hz, 2H), 8.86 (dd, J = 8.2 Hz, J = 1.2 Hz, 2H), 8.19 (s, 2H), 8.16 (dd, J = 8.2 Hz, 5.5 Hz, 2H), 6.50 (t, J = 6.3 Hz, 2H), 6.27 (d, J = 6.3 Hz, 2H), 6.01 (t, J = 5.9 Hz, 1H), 3.58 (t, J = 6.3 Hz, 2H), 2.66 (t, J = 6.6 Hz, 2H). ^{13}C NMR (100 MHz, D_2O) δ 169.9, 155.6, 146.4, 140.4, 131.0, 127.7, 126.7, 102.0, 88.7, 83.9, 81.0, 42.1, 38.9, 32.2. HPLC-ESI-MS (m/z): 239.6 [**1b** – H_2O]$^{2+}$ (calc m/z 239.5); 260.3 [**1b** – H_2O + CH_3CN]$^{2+}$ (calc m/z 260.0).

Figure S1. LC-ESI-MS of **1b**. Shown is the spectrum obtained at the indicated retention time.



*c. PAP-**1a** conjugate*

Papain (3.24 mg) in 20 mM phosphate buffer pH 7, 0.4 M NaCl (40 ml) and **1a** (1.2 mg, ca. 16 molar eq.) were mixed together and incubated overnight at room temperature without stirring. The solution was concentrated to 5 ml by ultrafiltration in a stirred cell (Millipore) equipped with an

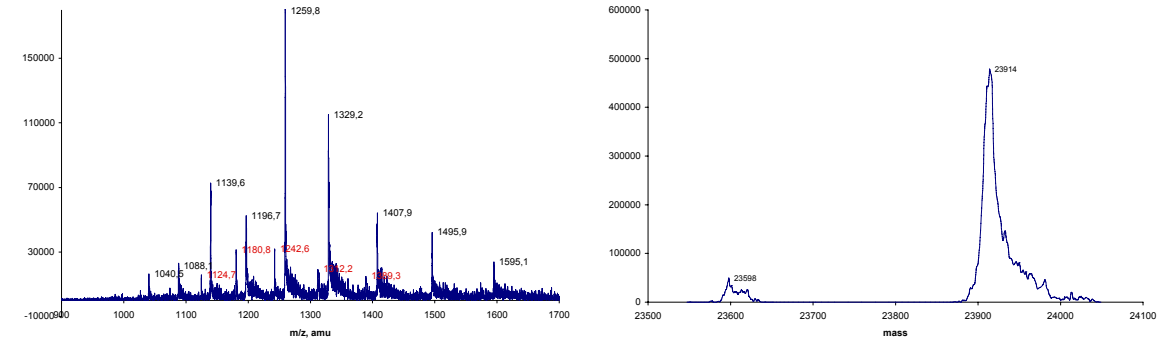
ultracell 5kD membrane (Millipore) and passed on a gel desalting column (Hiprep 26/10, Pharmacia) using 0.15 M NaCl at 5 ml/min as eluent. Fractions containing the protein were pooled and the solution was concentrated to 2 ml by ultrafiltration in a stirred cell (Millipore) equipped with an ultracell 5kD membrane (Millipore). The solution was eventually dialysed in water in a 7 kD dialysis tube (Novagen) for 40 h at 4°C.

*d. ESI-MS characterisation of PAP-**1a***

ESI-MS spectra were acquired on a triple quadrupole mass spectrometer API 3000 LC-MS/MS system (Applied Biosystems, PE Sciex) in positive-ion mode with the following parameters: declustering potential 20 V, capillary voltage 5000 V, source temperature 400°C. The protein sample (20 µl of a 0.4 mM solution acidified by addition of 5 µl 10% HCOOH) was introduced through the liquid chromatography system (Agilent 1100 series) without column into the turbo ionspray source using H_2O/MeOH (1:1) as eluent (0.2 mL/min). the mass spectrum containing multi-charged protein species was deconvoluted with the Magtran 1.03 software[v].

Figure S2. A) mass spectrum in ESI mode of PAP-**1a; B)** deconvoluted mass spectrum in ESI mode of PAP-**1a**

A **B**



MW = 23914 ± 4 : [PAP-**1a**] – Cl + HCOO
MW = 23597 ± 4 : [PAP-**1a**] – Ru(phen)Cl

B) Analytical data

a. X-ray crystallographic data of 1a•BF_4

The structure was solved by direct methods using the SIR97 programme, [vi] and then refined with full-matrix least-square methods based on F^2 (SHELX-97)[vii] with the aid of the WINGX[viii] programme. All non-hydrogen atoms were refined with anisotropic thermal parameters. H atoms were finally included in their calculated positions. A final refinement on F^2 with 5002 unique intensities and 307 parameters converged at $wR(F^2) = 0.0632$ ($R(F) = 0.0304$) for 4553 observed reflections with $I > 2\sigma(I)$. Deposition at the CCDC under number 742394.

Figure S3. ORTEP drawing of the molecular structure of **1a**•BF_4 with atoms numbering. Ellipsoids are shown at 40% probability.

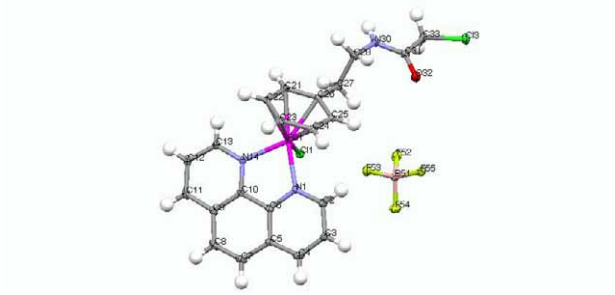


Table S2. Structural data

Empirical formula	$C_{22}\ H_{20}\ Cl_2\ N_3\ O\ Ru,\ B\ F_4$
Formula weight	601.19
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system, space group	monoclinic, P 2_1/c
Unit cell dimensions	a = 8.1828(3) Å, alpha = 90 ° b = 28.4447(10) Å, beta = 111.9220(10) ° c = 10.2133(4) Å, gamma = 90 °
Volume	2205.33(14) $Å^3$
Z, Calculated density	4 , 1.811 ($g.cm^{-3}$)
Absorption coefficient	1.009 mm^{-1}
F(000)	1200
Crystal size	0.56 x 0.1 x 0.08 mm
Theta range for data collection	3.44 to 27.44 °
h_min, h_max	-10 , 10
k_min, k_max	-36 , 33
l_min, l_max	-12 , 13
Reflections collected / unique	19047 / 5002 [R(int) = 0.0378]
Completeness to theta_max	0.991
Absorption correction type	multi-scan
Max. and min. transmission	0.922 , 0.757
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5002 / 0 / 307
Goodness-of-fit	1.082
Final R indices [I>2sigma(I)]	R_1 = 0.0304, wR_2 = 0.0632
R indices (all data)	R_1 = 0.0349, wR_2 = 0.0664
Largest diff. peak and hole	0.469 and -0.562 $e.A^{-3}$

Table S3. Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$ x 10^3). U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U(eq)
Ru1	0.36851(2)	0.112618(6)	0.84341(2)	0.01216(6)
Cl1	0.16755(7)	0.12873(2)	0.60692(6)	0.01961(13)
N1	0.3251(2)	0.18261(7)	0.8850(2)	0.0150(4)
C2	0.2099(3)	0.19829(9)	0.9383(3)	0.0189(5)
H2	0.1359	0.1763	0.9596	0.023
C3	0.1938(3)	0.24628(9)	0.9641(3)	0.0212(5)
H3	0.1122	0.2563	1.0046	0.025
C4	0.2966(3)	0.27856(9)	0.9306(3)	0.0223(5)
H4	0.2861	0.3111	0.9472	0.027
C5	0.4176(3)	0.26328(8)	0.8716(3)	0.0187(5)
C6	0.4284(3)	0.21464(8)	0.8518(2)	0.0146(5)
C7	0.5312(3)	0.29355(9)	0.8308(3)	0.0225(5)
H7	0.5252	0.3266	0.8425	0.027
C8	0.6457(3)	0.27645(9)	0.7765(3)	0.0234(6)
H8	0.7184	0.2976	0.7505	0.028
C9	0.6600(3)	0.22672(9)	0.7572(3)	0.0186(5)
C10	0.5505(3)	0.19620(8)	0.7960(3)	0.0155(5)
C11	0.7761(3)	0.20607(9)	0.7010(3)	0.0221(5)
H11	0.8513	0.2253	0.6718	0.027
C12	0.7800(3)	0.15792(9)	0.6888(3)	0.0207(5)
H12	0.8581	0.1436	0.6514	0.025
C13	0.6675(3)	0.13027(9)	0.7320(3)	0.0169(5)
H13	0.6726	0.0971	0.7244	0.02
N14	0.5539(2)	0.14848(7)	0.7832(2)	0.0140(4)
C21	0.4069(3)	0.03607(8)	0.8334(3)	0.0166(5)
H21	0.4226	0.0170.7626	0.02	
C22	0.5544(3)	0.05632(8)	0.9401(3)	0.0165(5)
H22	0.6686	0.0513	0.9389	0.02

C23	0.5350(3)	0.08393(8)	1.0489(3)	0.0186(5)
H23	0.6349	0.097	1.1215	0.022
C24	0.3637(3)	0.09149(9)	1.0466(3)	0.0191(5)
H24	0.3485	0.1102	1.1182	0.023
C25	0.2138(3)	0.07184(8)	0.9402(3)	0.0179(5)
H25	0.0998	0.0771	0.9415	0.021
C26	0.2344(3)	0.04434(8)	0.8319(3)	0.0162(5)
C27	0.0761(3)	0.02426(8)	0.7157(3)	0.0208(5)
H27A	0.1005	0.0209	0.6283	0.025
H27B	-0.0263	0.0455	0.6961	0.025
C28	0.0359(3)	-0.02374(9)	0.7635(3)	0.0238(6)
H28A	0.1381	-0.0448	0.7801	0.029
H28B	0.0194	-0.0201	0.8542	0.029
N30	-0.1206(3)	-0.04553(7)	0.6610(2)	0.0212(5)
H30	-0.1094	-0.0667	0.6021	0.025
C31	-0.2812(3)	-0.03377(8)	0.6553(3)	0.0184(5)
O32	-0.3094(2)	-0.00243(6)	0.72685(19)	0.0247(4)
C33	-0.4275(3)	-0.06132(9)	0.5449(3)	0.0204(5)
H33A	-0.3845	-0.0933	0.5375	0.024
H33B	-0.458	-0.0458	0.4521	0.024
Cl3	-0.62004(7)	-0.06558(2)	0.58596(7)	0.02315(14)
B51	-0.0225(4)	0.14831(10)	1.1509(3)	0.0197(6)
F52	-0.0838(2)	0.11714(5)	1.03638(16)	0.0269(4)
F53	0.16058(18)	0.14413(5)	1.21358(17)	0.0260(3)
F54	-0.0685(2)	0.19395(5)	1.10369(19)	0.0349(4)
F55	-0.09712(18)	0.13625(5)	1.24908(16)	0.0229(3)

Table S4. Anisotropic displacement parameters ($Å^2$). The anisotropic displacement factor exponent takes the form: $-2\ p^2\ [\ h^2\ a^{*2}\ U_{11} + ... + 2\ h\ k\ a^*\ b^*\ U_{12}]$.

Atom	U11	U22	U33	U23	U13	U12
Ru1	0.01139(9)	0.01106(10)	0.01509(11)	0.00079(7)	0.00616(7)	-0.00005(
Cl1	0.0181(3)	0.0211(3)	0.0198(3)	0.0012(2)	0.0072(2)	-0.0005(2
N1	0.0147(9)	0.0149(10)	0.0162(11)	0.0019(8)	0.0066(8)	0.0008(7
C2	0.0190(11)	0.0189(12)	0.0204(13)	0.0032(10)	0.0090(10)	0.0019(9
C3	0.0247(12)	0.0211(13)	0.0194(13)	0.0007(11)	0.0100(10)	0.0061(1
C4	0.0297(13)	0.0154(12)	0.0203(14)	0.0000(10)	0.0078(11)	0.0039(1
C5	0.0229(12)	0.0159(12)	0.0156(13)	0.0015(10)	0.0051(10)	-0.0001(9
C6	0.0166(10)	0.0136(11)	0.0127(12)	0.0021(9)	0.0043(9)	-0.0002(9
C7	0.0298(13)	0.0128(12)	0.0229(14)	0.0004(10)	0.0075(11)	-0.0038(1
C8	0.0264(13)	0.0194(13)	0.0236(14)	0.0044(11)	0.0084(11)	-0.0072(1
C9	0.0167(11)	0.0210(13)	0.0161(13)	0.0013(10)	0.0039(10)	-0.0044(9
C10	0.0157(10)	0.0150(11)	0.0148(12)	0.0006(9)	0.0044(9)	-0.0016(9
C11	0.0168(11)	0.0284(14)	0.0214(14)	0.0036(11)	0.0075(10)	-0.0059(1
C12	0.0150(11)	0.0302(14)	0.0188(13)	-0.0015(11)	0.0084(10)	-0.0023(1
C13	0.0147(10)	0.0195(12)	0.0156(12)	0.0002(10)	0.0047(9)	-0.0002(9
N14	0.0123(8)	0.0155(10)	0.0149(10)	0.0003(8)	0.0059(8)	-0.0005(7
C21	0.0199(11)	0.0102(11)	0.0209(13)	0.0004(10)	0.0090(10)	0.0004(9
C22	0.0151(10)	0.0144(11)	0.0212(13)	0.0067(10)	0.0082(9)	0.0029(9
C23	0.0203(11)	0.0163(12)	0.0164(13)	0.0078(10)	0.0036(10)	0.0024(9
C24	0.0282(13)	0.0162(12)	0.0178(13)	0.0057(10)	0.0140(11)	0.0042(1
C25	0.0179(11)	0.0153(12)	0.0242(14)	0.0061(10)	0.0124(10)	0.0004(9
C26	0.0179(11)	0.0110(11)	0.0198(13)	0.0044(10)	0.0071(10)	-0.0025(9
C27	0.0183(11)	0.0167(12)	0.0248(14)	0.0015(10)	0.0051(10)	-0.0039(9
C28	0.0142(11)	0.0180(12)	0.0325(16)	0.0040(11)	0.0012(11)	-0.0022(9
N30	0.0162(9)	0.0150(10)	0.0309(13)	-0.0035(9)	0.0069(9)	-0.0018(8
C31	0.0198(11)	0.0157(12)	0.0207(13)	0.0017(10)	0.0086(10)	-0.0016(9
O32	0.0218(9)	0.0287(10)	0.0247(10)	-0.0070(8)	0.0101(8)	-0.0032(7
C33	0.0145(11)	0.0248(13)	0.0231(14)	-0.0048(11)	0.0085(10)	-0.0023(9
Cl3	0.0177(3)	0.0292(3)	0.0242(3)	-0.0050(3)	0.0097(2)	-0.0055(2
B51	0.0203(13)	0.0167(14)	0.0254(16)	-0.0020(12)	0.0125(12)	0.0004(1

F52	0.0240(8)	0.0342(9)	0.0231(9)	-0.0084(7)	0.0096(7)	0.0000(6
F53	0.0189(7)	0.0307(9)	0.0303(9)	-0.0065(7)	0.0114(6)	-0.0032(6
F54	0.0452(10)	0.0222(8)	0.0481(11)	0.0104(8)	0.0298(9)	0.0094(7
F55	0.0233(7)	0.0240(8)	0.0262(8)	-0.0011(6)	0.0147(6)	0.0003(6

Table S5. Bond lengths [Å]

Ru1 - N1	2.0934(19)	C13 - N14	1.330(3)
Ru1 - N14	2.1015(19)	C13 - H13	0.95
Ru1 - C24	2.175(2)	C21 - C22	1.412(3)
Ru1 - C22	2.175(2)	C21 - C26	1.426(3)
Ru1 - C23	2.189(2)	C21 - H21	0.95
Ru1 - C25	2.205(2)	C22 - C23	1.417(4)
Ru1 - C21	2.208(2)	C22 - H22	0.95
Ru1 - C26	2.212(2)	C23 - C24	1.410(3)
Ru1 - Cl1	2.4046(6)	C23 - H23	0.95
N1 - C2	1.330(3)	C24 - C25	1.415(3)
N1 - C6	1.368(3)	C24 - H24	0.95
C2 - C3	1.406(3)	C25 - C26	1.415(3)
C2 - H2	0.95	C25 - H25	0.95
C3 - C4	1.372(4)	C26 - C27	1.505(3)
C3 - H3	0.95	C27 - C28	1.526(3)
C4 - C5	1.406(4)	C27 - H27A	0.99
C4 - H4	0.95	C27 - H27B	0.99
C5 - C6	1.406(3)	C28 - N30	1.456(3)
C5 - C7	1.439(3)	C28 - H28A	0.99
C6 - C10	1.423(3)	C28 - H28B	0.99
C7 - C8	1.345(4)	N30 - C31	1.336(3)
C7 - H7	0.95	N30 - H30	0.88
C8 - C9	1.439(4)	C31 - O32	1.227(3)
C8 - H8	0.95	C31 - C33	1.520(3)
C9 - C10	1.406(3)	C33 - Cl3	1.779(2)
C9 - C11	1.408(4)	C33 - H33A	0.99
C10 - N14	1.365(3)	C33 - H33B	0.99
C11 - C12	1.377(4)	B51 - F54	1.387(3)
C11 - H11	0.95	B51 - F55	1.397(3)
C12 - C13	1.402(3)	B51 - F53	1.397(3)
C12 - H12	0.95	B51 - F52	1.403(3)

Table S6. Angles [°]

N1 - Ru1 - N14	78.07(7)	N14 - C13 - C12	122.9(2)
N1 - Ru1 - C24	90.26(9)	N14 - C13 - H13	118.5
N14 - Ru1 - C24	133.26(9)	C12 - C13 - H13	118.5
N1 - Ru1 - C22	138.67(8)	C13 - N14 - C10	117.8(2)
N14 - Ru1 - C22	91.79(8)	C13 - N14 - Ru1	127.80(16)
C24 - Ru1 - C22	67.79(9)	C10 - N14 - Ru1	114.35(15)
N1 - Ru1 - C23	104.60(9)	C22 - C21 - C26	119.9(2)
N14 - Ru1 - C23	101.67(8)	C22 - C21 - Ru1	69.96(13)
C24 - Ru1 - C23	37.69(9)	C26 - C21 - Ru1	71.35(13)
C22 - Ru1 - C23	37.90(9)	C22 - C21 - H21	120.1
N1 - Ru1 - C25	103.90(8)	C26 - C21 - H21	120.1
N14 - Ru1 - C25	169.95(8)	Ru1 - C21 - H21	131.4
C24 - Ru1 - C25	37.69(9)	C21 - C22 - C23	121.2(2)
C22 - Ru1 - C25	80.22(9)	C21 - C22 - Ru1	72.47(13)
C23 - Ru1 - C25	68.28(9)	C23 - C22 - Ru1	71.60(13)
N1 - Ru1 - C21	170.14(8)	C21 - C22 - H22	119.4
N14 - Ru1 - C21	109.52(8)	C23 - C22 - H22	119.4
C24 - Ru1 - C21	79.95(9)	Ru1 - C22 - H22	128.9
C22 - Ru1 - C21	37.57(9)	C24 - C23 - C22	118.2(2)
C23 - Ru1 - C21	68.19(9)	C24 - C23 - Ru1	70.59(14)
C25 - Ru1 - C21	67.51(9)	C22 - C23 - Ru1	70.50(13)

N1 - Ru1 - C26	136.68(8)	C24 - C23 - H23	120.9
N14 - Ru1 - C26	143.96(8)	C22 - C23 - H23	120.9
C24 - Ru1 - C26	67.83(9)	Ru1 - C23 - H23	130.4
C22 - Ru1 - C26	68.07(9)	C23 - C24 - C25	121.6(2)
C23 - Ru1 - C26	80.93(9)	C23 - C24 - Ru1	71.72(14)
C25 - Ru1 - C26	37.38(9)	C25 - C24 - Ru1	72.30(14)
C21 - Ru1 - C26	37.63(8)	C23 - C24 - H24	119.2
N1 - Ru1 - Cl1	85.32(6)	C25 - C24 - H24	119.2
N14 - Ru1 - Cl1	84.92(5)	Ru1 - C24 - H24	129.3
C24 - Ru1 - Cl1	139.63(7)	C24 - C25 - C26	119.8(2)
C22 - Ru1 - Cl1	134.13(7)	C24 - C25 - Ru1	70.01(13)
C23 - Ru1 - Cl1	168.97(7)	C26 - C25 - Ru1	71.59(13)
C25 - Ru1 - Cl1	105.01(7)	C24 - C25 - H25	120.1
C21 - Ru1 - Cl1	101.36(7)	C26 - C25 - H25	120.1
C26 - Ru1 - Cl1	88.54(6)	Ru1 - C25 - H25	130.9
C2 - N1 - C6	118.4(2)	C25 - C26 - C21	119.3(2)
C2 - N1 - Ru1	127.00(16)	C25 - C26 - C27	120.5(2)
C6 - N1 - Ru1	114.57(15)	C21 - C26 - C27	120.2(2)
N1 - C2 - C3	122.2(2)	C25 - C26 - Ru1	71.03(13)
N1 - C2 - H2	118.9	C21 - C26 - Ru1	71.02(13)
C3 - C2 - H2	118.9	C27 - C26 - Ru1	129.71(17)
C4 - C3 - C2	119.6(2)	C26 - C27 - C28	108.2(2)
C4 - C3 - H3	120.2	C26 - C27 - H27A	110.1
C2 - C3 - H3	120.2	C28 - C27 - H27A	110.1
C3 - C4 - C5	119.7(2)	C26 - C27 - H27B	110.1
C3 - C4 - H4	120.2	C28 - C27 - H27B	110.1
C5 - C4 - H4	120.2	H27A - C27 - H27B	108.4
C6 - C5 - C4	117.3(2)	N30 - C28 - C27	112.8(2)
C6 - C5 - C7	117.7(2)	N30 - C28 - H28A	109
C4 - C5 - C7	125.0(2)	C27 - C28 - H28A	109
N1 - C6 - C5	122.8(2)	N30 - C28 - H28B	109
N1 - C6 - C10	116.4(2)	C27 - C28 - H28B	109
C5 - C6 - C10	120.8(2)	H28A - C28 - H28B	107.8
C8 - C7 - C5	121.9(2)	C31 - N30 - C28	120.8(2)
C8 - C7 - H7	119.1	C31 - N30 - H30	119.6
C5 - C7 - H7	119.1	C28 - N30 - H30	119.6
C7 - C8 - C9	121.1(2)	O32 - C31 - N30	123.8(2)
C7 - C8 - H8	119.4	O32 - C31 - C33	123.0(2)
C9 - C8 - H8	119.4	N30 - C31 - C33	113.1(2)
C10 - C9 - C11	117.1(2)	C31 - C33 - Cl3	112.45(18)
C10 - C9 - C8	118.3(2)	C31 - C33 - H33A	109.1
C11 - C9 - C8	124.6(2)	Cl3 - C33 - H33A	109.1
N14 - C10 - C9	123.3(2)	C31 - C33 - H33B	109.1
N14 - C10 - C6	116.6(2)	Cl3 - C33 - H33B	109.1
C9 - C10 - C6	120.1(2)	H33A - C33 - H33B	107.8
C12 - C11 - C9	119.6(2)	F54 - B51 - F55	110.2(2)
C12 - C11 - H11	120.2	F54 - B51 - F53	110.1(2)
C9 - C11 - H11	120.2	F55 - B51 - F53	109.4(2)
C11 - C12 - C13	119.3(2)	F54 - B51 - F52	109.6(2)
C11 - C12 - H12	120.4	F55 - B51 - F52	109.1(2)
C13 - C12 - H12	120.4	F53 - B51 - F52	108.4(2)

Table S7. Torsion angles [°]

N14 - Ru1 - N1 - C2	-179.0(2)	N1 - Ru1 - C22 - C21	165.62(13)
C24 - Ru1 - N1 - C2	-44.6(2)	N14 - Ru1 - C22 - C21	-120.50(14)
C22 - Ru1 - N1 - C2	-100.0(2)	C24 - Ru1 - C22 - C21	102.80(16)
C23 - Ru1 - N1 - C2	-79.8(2)	C23 - Ru1 - C22 - C21	132.7(2)
C25 - Ru1 - N1 - C2	-9.1(2)	C25 - Ru1 - C22 - C21	65.64(15)
C26 - Ru1 - N1 - C2	12.4(3)	C26 - Ru1 - C22 - C21	28.76(14)
Cl1 - Ru1 - N1 - C2	95.3(2)	Cl1 - Ru1 - C22 - C21	-35.84(17)

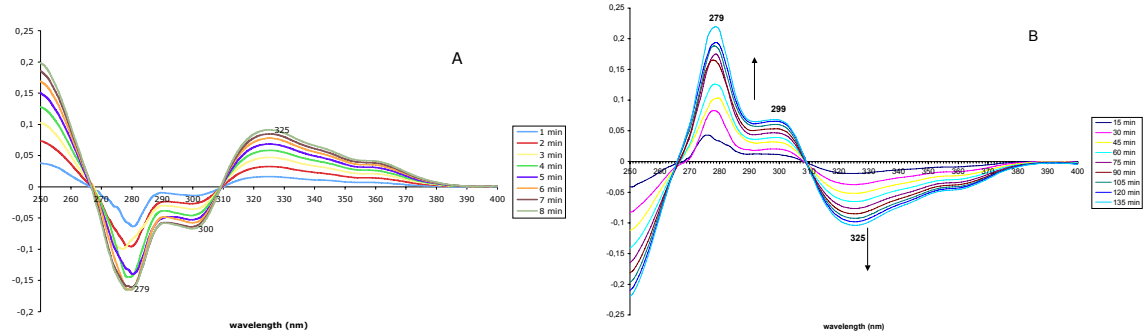
N14 - Ru1 - N1 - C6	1.35(16)	N1 - Ru1 - C22 - C23	32.94(19)
C24 - Ru1 - N1 - C6	135.74(17)	N14 - Ru1 - C22 - C23	106.82(14)
C22 - Ru1 - N1 - C6	80.3(2)	C24 - Ru1 - C22 - C23	-29.88(14)
C23 - Ru1 - N1 - C6	100.48(17)	C25 - Ru1 - C22 - C23	-67.04(14)
C25 - Ru1 - N1 - C6	171.24(16)	C21 - Ru1 - C22 - C23	-132.7(2)
C26 - Ru1 - N1 - C6	-167.30(15)	N1 - Ru1 - C23 - C22	-158.22(13)
Cl1 - Ru1 - N1 - C6	-84.44(16)	N14 - Ru1 - C23 - C22	-77.68(14)
C6 - N1 - C2 - C3	-1.4(3)	C24 - Ru1 - C23 - C22	131.0(2)
Ru1 - N1 - C2 - C3	178.92(18)	C25 - Ru1 - C23 - C22	102.37(15)
N1 - C2 - C3 - C4	1.6(4)	C21 - Ru1 - C23 - C22	28.87(13)
C2 - C3 - C4 - C5	-0.4(4)	C26 - Ru1 - C23 - C22	65.75(14)
C3 - C4 - C5 - C6	-0.9(4)	Cl1 - Ru1 - C23 - C22	48.3(4)
C3 - C4 - C5 - C7	179.4(2)	C22 - C23 - C24 - C25	0.8(3)
C2 - N1 - C6 - C5	0.0(3)	Ru1 - C23 - C24 - C25	54.6(2)
Ru1 - N1 - C6 - C5	179.72(18)	C22 - C23 - C24 - Ru1	-53.81(19)
C2 - N1 - C6 - C10	179.6(2)	N1 - Ru1 - C24 - C23	-113.98(15)
Ru1 - N1 - C6 - C10	-0.7(3)	N14 - Ru1 - C24 - C23	-40.22(19)
C4 - C5 - C6 - N1	1.1(4)	C22 - Ru1 - C24 - C23	30.04(14)
C7 - C5 - C6 - N1	-179.1(2)	C25 - Ru1 - C24 - C23	133.2(2)
C4 - C5 - C6 - C10	-178.4(2)	C21 - Ru1 - C24 - C23	67.19(15)
C7 - C5 - C6 - C10	1.3(3)	C26 - Ru1 - C24 - C23	104.41(16)
C6 - C5 - C7 - C8	-0.6(4)	Cl1 - Ru1 - C24 - C23	162.96(11)
C4 - C5 - C7 - C8	179.1(3)	N1 - Ru1 - C24 - C25	112.78(14)
C5 - C7 - C8 - C9	-0.2(4)	N14 - Ru1 - C24 - C25	-173.46(13)
C7 - C8 - C9 - C10	0.2(4)	C22 - Ru1 - C24 - C25	-103.20(15)
C7 - C8 - C9 - C11	179.9(2)	C23 - Ru1 - C24 - C25	-133.2(2)
C11 - C9 - C10 - N14	0.8(4)	C21 - Ru1 - C24 - C25	-66.05(14)
C8 - C9 - C10 - N14	-179.5(2)	C26 - Ru1 - C24 - C25	-28.82(14)
C11 - C9 - C10 - C6	-179.2(2)	Cl1 - Ru1 - C24 - C25	29.72(19)
C8 - C9 - C10 - C6	0.5(3)	C23 - C24 - C25 - C26	-0.8(4)
N1 - C6 - C10 - N14	-0.9(3)	Ru1 - C24 - C25 - C26	53.5(2)
C5 - C6 - C10 - N14	178.7(2)	C23 - C24 - C25 - Ru1	-54.3(2)
N1 - C6 - C10 - C9	179.1(2)	N1 - Ru1 - C25 - C24	-71.77(15)
C5 - C6 - C10 - C9	-1.3(3)	N14 - Ru1 - C25 - C24	28.4(5)
C10 - C9 - C11 - C12	-1.0(4)	C22 - Ru1 - C25 - C24	66.16(15)
C8 - C9 - C11 - C12	179.2(2)	C23 - Ru1 - C25 - C24	28.65(14)
C9 - C11 - C12 - C13	0.2(4)	C21 - Ru1 - C25 - C24	103.11(15)
C11 - C12 - C13 - N14	0.9(4)	C26 - Ru1 - C25 - C24	132.7(2)
C12 - C13 - N14 - C10	-1.2(3)	Cl1 - Ru1 - C25 - C24	-160.59(12)
C12 - C13 - N14 - Ru1	176.80(17)	N1 - Ru1 - C25 - C26	155.57(13)
C9 - C10 - N14 - C13	0.3(3)	N14 - Ru1 - C25 - C26	-104.3(5)
C6 - C10 - N14 - C13	-179.7(2)	C24 - Ru1 - C25 - C26	-132.7(2)
C9 - C10 - N14 - Ru1	-177.95(18)	C22 - Ru1 - C25 - C26	-66.50(14)
C6 - C10 - N14 - Ru1	2.1(3)	C23 - Ru1 - C25 - C26	-104.00(15)
N1 - Ru1 - N14 - C13	-179.9(2)	C21 - Ru1 - C25 - C26	-29.54(13)
C24 - Ru1 - N14 - C13	101.2(2)	Cl1 - Ru1 - C25 - C26	66.76(13)
C22 - Ru1 - N14 - C13	40.5(2)	C24 - C25 - C26 - C21	1.3(3)
C23 - Ru1 - N14 - C13	77.4(2)	Ru1 - C25 - C26 - C21	54.02(19)
C25 - Ru1 - N14 - C13	77.7(5)	C24 - C25 - C26 - C27	-178.3(2)
C21 - Ru1 - N14 - C13	6.7(2)	Ru1 - C25 - C26 - C27	-125.6(2)
C26 - Ru1 - N14 - C13	-13.1(3)	C24 - C25 - C26 - Ru1	-52.8(2)
Cl1 - Ru1 - N14 - C13	-93.6(2)	C22 - C21 - C26 - C25	-1.7(3)
N1 - Ru1 - N14 - C10	-1.83(16)	Ru1 - C21 - C26 - C25	-54.02(19)
C24 - Ru1 - N14 - C10	-80.73(19)	C22 - C21 - C26 - C27	177.9(2)
C22 - Ru1 - N14 - C10	-141.40(17)	Ru1 - C21 - C26 - C27	125.6(2)
C23 - Ru1 - N14 - C10	-104.50(17)	C22 - C21 - C26 - Ru1	52.3(2)
C25 - Ru1 - N14 - C10	-104.2(5)	N1 - Ru1 - C26 - C25	-35.81(19)
C21 - Ru1 - N14 - C10	-175.28(16)	N14 - Ru1 - C26 - C25	163.30(14)
C26 - Ru1 - N14 - C10	164.90(16)	C24 - Ru1 - C26 - C25	29.05(14)
Cl1 - Ru1 - N14 - C10	84.44(16)	C22 - Ru1 - C26 - C25	103.03(15)

N14 - Ru1 - C21 - C22	66.03(15)	C23 - Ru1 - C26 - C25	65.89(14)
C24 - Ru1 - C21 - C22	-66.48(15)	C21 - Ru1 - C26 - C25	131.7(2)
C23 - Ru1 - C21 - C22	-29.10(14)	Cl1 - Ru1 - C26 - C25	-117.40(13)
C25 - Ru1 - C21 - C22	-103.69(16)	N1 - Ru1 - C26 - C21	-167.55(13)
C26 - Ru1 - C21 - C22	-133.0(2)	N14 - Ru1 - C26 - C21	31.6(2)
Cl1 - Ru1 - C21 - C22	154.62(13)	C24 - Ru1 - C26 - C21	-102.70(16)
N14 - Ru1 - C21 - C26	-160.93(14)	C22 - Ru1 - C26 - C21	-28.71(14)
C24 - Ru1 - C21 - C26	66.56(15)	C23 - Ru1 - C26 - C21	-65.85(15)
C22 - Ru1 - C21 - C26	133.0(2)	C25 - Ru1 - C26 - C21	-131.7(2)
C23 - Ru1 - C21 - C26	103.94(16)	Cl1 - Ru1 - C26 - C21	110.85(14)
C25 - Ru1 - C21 - C26	29.35(14)	N1 - Ru1 - C26 - C27	78.5(3)
Cl1 - Ru1 - C21 - C26	-72.34(14)	N14 - Ru1 - C26 - C27	-82.4(3)
C26 - C21 - C22 - C23	1.7(3)	C24 - Ru1 - C26 - C27	143.4(2)
Ru1 - C21 - C22 - C23	54.6(2)	C22 - Ru1 - C26 - C27	-142.7(3)
C26 - C21 - C22 - Ru1	-53.0(2)	C23 - Ru1 - C26 - C27	-179.8(2)
C26 - Ru1 - C22 - C23	-103.92(15)	C25 - Ru1 - C26 - C27	114.3(3)
Cl1 - Ru1 - C22 - C23	-168.52(11)	C21 - Ru1 - C26 - C27	-113.9(3)
C21 - C22 - C23 - C24	-1.2(3)	Cl1 - Ru1 - C26 - C27	-3.1(2)
Ru1 - C22 - C23 - C24	53.85(19)	C25 - C26 - C27 - C28	-88.8(3)
C21 - C22 - C23 - Ru1	-55.0(2)	C21 - C26 - C27 - C28	91.6(3)
N1 - Ru1 - C23 - C24	70.76(15)	Ru1 - C26 - C27 - C28	-178.75(18)
N14 - Ru1 - C23 - C24	151.30(14)	C26 - C27 - C28 - N30	177.4(2)
C22 - Ru1 - C23 - C24	-131.0(2)	C27 - C28 - N30 - C31	-82.0(3)
C25 - Ru1 - C23 - C24	-28.65(14)	C28 - N30 - C31 - O32	5.1(4)
C21 - Ru1 - C23 - C24	-102.15(16)	C28 - N30 - C31 - C33	-178.2(2)
C26 - Ru1 - C23 - C24	-65.27(15)	O32 - C31 - C33 - Cl3	-28.9(3)
Cl1 - Ru1 - C23 - C24	-82.7(4)	N30 - C31 - C33 - Cl3	154.29(19)

*c. Kinetic plots of aquation of **1a** and anation of **1b***

Measurement of aquation and anation rate constants was carried out from a previously described experimental procedure.[ix] Anation of **1b**: An aqueous solution of **1b** (50 ul ; 1 mM) was mixed with NaCl (5 M ; 1, 2, 5 or 10 ul) and water was added to a final volume of 500 ul. The uv spectrum was recorded every min for 15 min between 250 and 400 nm (fig. S4). Aquation of **1a**: A solution of **1a** in DMSO (50 ul ; 1 mM) was mixed with water (450 ul). The uv spectrum between 250 and 400 nm was recorded every 15 min for 12 h.

Figure S4. A. Time evolution of uv difference spectra for the anation of **1b** at room temperature. [**1b**] = 0.1 mM, [NaCl] = 50 mM. B. Time evolution of uv difference spectra for the aquation of **1a** at room temperature. [**1a**] = 0.1 mM



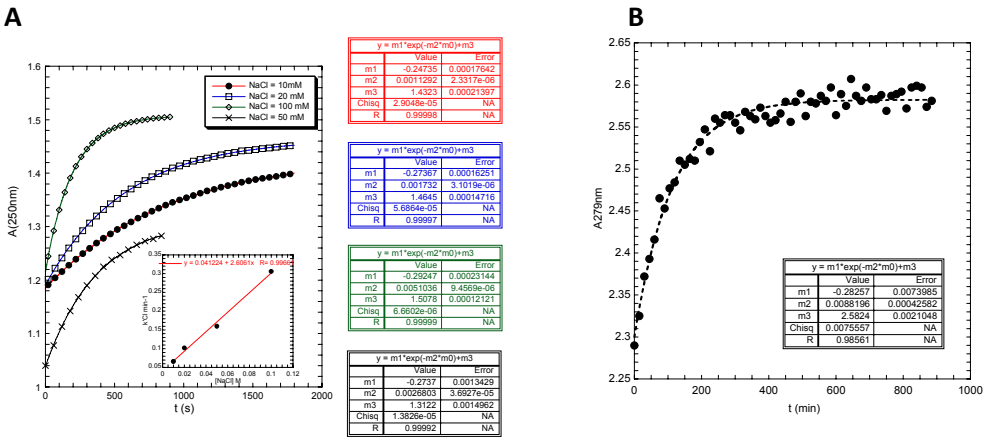
The pseudo-first order rates constant of anation of **1b** k'_{Cl} were determined by plotting the absorbance at 250 nm as a function of time (fig. S5, A). Data were fitted to a first order law equation (1) by non linear regression analysis with Kaleidagraph.

(1) $A = C_0 + C_1 e^{-kt}$

where A is A_{250} at time t, C_0 and C_1 are constants and k is the pseudo first order rate constant k'_{Cl}. The second-order rate constant of anation of **1b** k_{Cl} was calculated from the slope of the plot of the pseudo-first-order rate constants k'_{Cl} vs. $[Cl^-]$ (fig. S5, A, inset).

The first order rate constant of hydrolysis of **1a** k_{H2O} was determined by plotting the absorbance at 279 nm as a function of time (fig. S5, B). Data were fitted to a first order law equation (1) by non linear regression analysis with Kaleidagraph to yield the first order rate constant k_{H2O}.

Figure S5. A. Time-dependence of the absorbance at 250 nm for the anation of **1b**. The lines represent computer-fits giving the pseudo-first order rate constants k'_{Cl}. Inset : Calculation of the second order rate constant of anation k_{Cl}. B. Time-dependence of the absorbance at 279 nm for the aquation of 1a. The line represents computer fit giving the first order rate constant k_{H2O}



The equilibrium constant of the hydrolysis reaction K_{aq} was calculated from the k_{H2O} / k_{Cl} ratio.

k_{Cl} = 2.6 M^{-1} min^{-1} ; k_{H2O} = 0.0088 min^{-1} ; K_{aq} = 3.5 mM

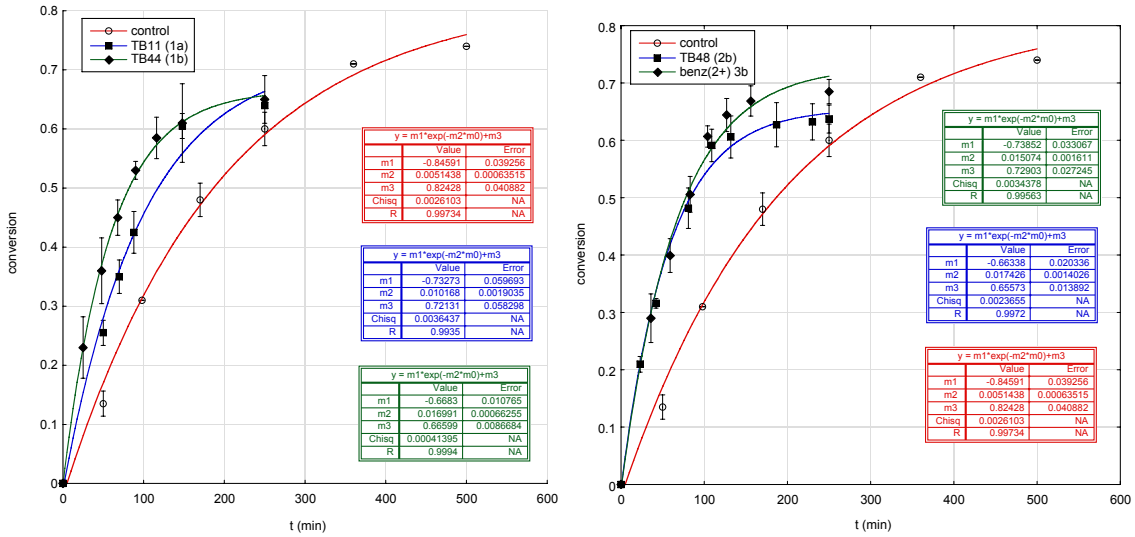
D) Catalysis experiments

a. General procedure

Acrolein (46 µmol, 3 µl) was dissolved in 1 ml of deionised water placed in a glass tube. The tube was placed in a cold bath cooled to 2°C and left to equilibrate for 1 h before the addition of CpH (460 µmol, 38 µl). The catalyst was added to the solution and the mixture was stirred. The formation of bicyclo[2.2.1]hept-5-ene-2-carboxaldehyde (exo + endo isomers) was monitored by GC analysis during 250 min by periodical removal of 50 µl aliquots followed by extraction with diethyl ether (0.1 ml) and using decane as an internal standard.

*b. Kinetic plots of catalysis experiments with **1a**, **1b-3b** at 10 mol%*

Figure S6. Kinetic plots of the DA reaction between acrolein and cyclopentadiene in water at 2°C. Data points were fitted to a pseudo-first order law equation by non-linear regression analysis using Kaleidagraph.



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